

## Fatty acids as phase change materials: A review



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### ABSTRACT

Fatty acids as phase change materials have attracted much attention for their various applications in building energy efficiency, solar heating systems and air-conditioning systems. After summarizing the basic characteristics of fatty acids, eutectic mixtures of fatty acids and fatty acid esters, as well as the preparation and characteristics of fatty acid composites as phase change materials (PCMs), this paper analyzes the thermal reliability and stability of fatty acids as PCMs and their heat transfer characteristics in a unit which is followed by an introduction to the energy storage systems of three kinds of fatty acids as PCMs. Besides, it also points out the future research direction of fatty acids as PCMs as a solution of the insufficiency and flaws of current researches.

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### Contents

1. Introduction . . . . .	483
2. Fatty acids as PCMs . . . . .	483
2.1. Pure fatty acids . . . . .	483
2.2. Eutectic mixtures of binary fatty acids . . . . .	483
2.3. Fatty acid esters . . . . .	484
2.4. Other mixtures of fatty acids . . . . .	486
2.5. Thermal reliability of fatty acids . . . . .	486
2.6. Heat transfer characteristics of fatty acids in a thermal energy storage unit . . . . .	487
3. Fatty acid composites as PCMs . . . . .	489
3.1. Composite PCMs with enhanced heat-conduction property . . . . .	489
3.2. Form-stable composite PCMs . . . . .	490
3.2.1. PCMs prepared in porous matrix by absorption . . . . .	490
3.2.2. Fatty acid and polymer mixtures as PCMs . . . . .	491
3.2.3. Electrospun composite PCMs . . . . .	492
3.2.4. Microencapsulated composite PCMs . . . . .	492
4. Fatty acids as PCMs for energy storage system . . . . .	493
4.1. Wallboard with PCM energy storage system . . . . .	493
4.2. Solar heat storage and photovoltaic system . . . . .	493
4.3. Condensing heat recovery of the air conditioning system . . . . .	494
5. Discussions and conclusions . . . . .	495
5.1. Eutectic mixture of fatty acids . . . . .	495
5.2. Thermal reliability and stability of fatty acids . . . . .	496
5.3. The increase of thermal conductivity and the setting of PCMs . . . . .	496
5.4. Phase change energy accumulator . . . . .	496
5.5. Thermal properties of fatty acids . . . . .	496
5.6. Applications of the fatty acids . . . . .	496

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Acknowledgments . . . . .	496
References . . . . .	496

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## 1. Introduction

In recent years, with the rapid economic development, energy shortage and environmental issues have become increasingly serious. Therefore, it is an important topic to improve energy utilization efficiency and protect environment. Energy storage is an essential method to match the thermal energy supply and demand in time or space. Latent heat thermal energy storage (LHTES) can achieve a higher energy storage density, a smaller size of the system and a narrower temperature range during the melting and freezing process of phase change materials (PCMs). PCMs have attracted much attention for their various applications in building energy efficiency, solar heating systems and air-conditioning systems [1–4].

At present, a large number of inorganic, organic and their mixtures PCMs have been studied. Among all investigated PCMs, fatty acids have many superior properties, including proper melting temperature range, high heat capacity, congruent melting, little or no supercooling during phase transition, lower vapor pressure, non-toxic, non-corrosive to metal containers, good chemical and thermal stability, low cost, non-flammability and small volume change [5–10]. In the researches of the fatty acids as PCMs, it is found that, two or more fatty acids can be mixed to form the eutectic mixture with a lower phase change temperature. It is also found that fatty acids esters can be synthesized via esterification reaction, and fatty acid composite PCMs also can be prepared through different ways. These fatty acids derivatives have enriched the application of fatty acids.

In this paper, a review of the literatures on the thermal properties, derivatives, composites, applications, and limitations of fatty acids as PCM is presented.

## 2. Fatty acids as PCMs

### 2.1. Pure fatty acids

Phase change temperature and latent heat are the two basic parameters of phase change materials (PCMs); therefore, many researchers have tested the two parameters of fatty acids as PCMs. This paper summarizes the test results of the phase change temperature and latent heat of fatty acids as PCMs as indicated in Table 1. Since the phase change temperature and latent heat of PCMs tend to be influenced by individual experimental conditions such as temperature, purity, and the accuracy of analytical instruments etc., literature data in Table 1 are slightly different from each other [5]. In the literature reviewed, almost no research has been done about the unsaturated acids as PCMs or the chemical structure of saturated and unsaturated acids and the influence of chemical structure on thermal properties. Besides, the research on fatty acids as PCMs is mainly on the phase change temperature and latent heat, thermal conductivity, heat transfer behavior of saturated acids with the carbon number of 10–18. In general, it is easy to find that, the phase change temperature and latent heat of saturated fatty acids are increasing with the increase of the carbon chain length. Besides, the application of fatty acids as PCMs is influenced by other physical and thermal properties of fatty acids as PCMs such as their density, specific heat and thermal conductivity listed in Table 2.

### 2.2. Eutectic mixtures of binary fatty acids

The eutectic temperature is the lowest melting temperature of a mixture of two or more components, and such mixture is a eutectic

mixture which features the same stability of a single component. The eutectic mixtures of fatty acids as PCMs have expanded the phase change temperature range and thus the engineering application of fatty acids as PCMs. The properties of fatty acids as PCMs are listed in Table 3 as a summary of public literatures.

Generally, a eutectic mixture of fatty acids is prepared by slowly cooling down uniformly mixed two kinds of fatty acids melted with different proportions. The mass ratio, phase change temperature and latent heat of the eutectic mixture are obtained via the differential scanning calorimeter (DSC) test. Considering the complexity of obtaining the mass ratio via experiments, Zhang et al. [36] analyzed a (quasi) eutectic based on the “second law of thermodynamics” and “phase equilibrium theory” and obtained the relation between the melting temperature, latent heat and component physical properties of the (quasi) eutectic, providing a theoretical guidance for predicting the melting temperature and latent heat and determining the optimal mass ratio of eutectic mixtures such as the eutectic mixtures of fatty acids. For a binary mixture with balanced phase change medium, the formulas for calculating the liquidus are shown below:

$$\begin{cases} -H_A(T_m-T_A)/T_A+RT_m \ln(1-X_A)+G_{A, ex}=0 \\ -H_B(T_m-T_B)/T_B+RT_m \ln(1-X_B)+G_{B, ex}=0 \end{cases} \quad (1)$$

In particular, for fatty acids,  $G_{A, ex}=G_{B, ex}=0$  is a very good approximation, therefore, the liquidus formula of component  $i$  is as below:

$$T_m = [1/T_i - R \ln X_i/H_i]^{-1} \quad (i = A, B) \quad (2)$$

where  $T_m$  is the melting temperature of the mixture,  $K$ ;  $T_i$ , the melting temperature of the  $i$ th component,  $K$ ;  $X_i$ , the mole fraction of the  $i$ th component;  $H_i$ , the latent heat of the  $i$ th component,  $J \text{ mol}^{-1}$ ; and  $R$ , gas constant,  $8.315 \text{ J mol}^{-1} \text{ K}^{-1}$ . By virtue of the formula above, the phase diagram of a binary eutectic can be drawn, and corresponding eutectic points can be determined.

The formula for calculating the melting enthalpy of a (quasi) eutectic is shown below:

$$H_m = T_m \sum_{i=1}^n [X_i H_i/T_i + X_i (C_{PLi} - C_{PSi}) \ln(T_m/T_i)] \quad (3)$$

where  $H_m$  is the latent heat of the mixture,  $J \text{ mol}^{-1}$ ;  $C_{PLi}$ , the specific heat at constant pressure of the  $i$ th component in the liquid state, and  $C_{PSi}$  the specific heat at constant pressure of the  $i$ th component in the solid state.

If the molecular weight of every component is big enough, Eq. (3) can be simplified as Eq. (4). The error of the formula for latent heat is rather small due to ignoring the sensible heat. As for the long-chain organic compounds, the error is less than 4%.

$$H_m = T_m \sum_{i=1}^n (X_i H_i/T_i) \quad (4)$$

With the same formula above, Yuan et al. [37] verified the mass ratio, melting temperature and melting enthalpy of the binary eutectic mixture mentioned in literature [19], and predicted the phase change temperature and phase change enthalpy of 15 eutectic mixtures of fatty acids via theoretical calculation. The calculation results show that the calculated values agree well with those of the previous experimental values. For the 15 eutectic mixtures of fatty acids, the minimum and maximum melting temperatures are 10.2 and 51.5 °C respectively, and the minimum and maximum latent heat values are 138.6 and 187.5 J/g respectively. The eutectic mixtures of fatty acids are

**Table 1**

Phase change temperature and latent heat of fatty acids.

Fatty acid	Melting temperature (°C)	Melting latent heat (J/g)	Freezing temperature (°C)	Freezing latent heat (J/g)	Purity	Reference
Caprylic acid $\text{CH}_3(\text{CH}_2)_6\text{COOH}$	16.1	144.2	–	–	> 99.9%	[11]
Capric acid $\text{CH}_3(\text{CH}_2)_8\text{COOH}$	29.62	139.77	25.57	140.12	CR	[12]
	30.64	155.46	–	–	CR	[13]
	31.5	155.5	–	–	CR	[14]
	32	152.7	–	–	–	[15]
	32.1	168.77	–	–	CR	[16]
	32.14	156.40	32.53	154.24	98%	[17]
Lauric acid $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$	$42.14 \pm 0.09$	$190.12 \pm 1.21$	$42.20 \pm 0.11$	$194.23 \pm 1.63$	> 98%	[18]
	42.4	186.4	–	–	98%	[19]
	42.46	176.6	–	–	97%	[20]
	42.6	176.6	–	–	98%	[21]
	42.6	211.6	–	–	97%	[8]
	42.91	175.83	–	–	CR	[13]
	43.55	184.29	39.78	184.73	98%	[22]
	44	175.8	–	–	CR	[14]
	44	177.4	–	–	–	[15]
	44.02	182.3	42.09	182.4	–	[23]
	44.32	179.85	41.72	180.51	RG	[24]
	44.33	217.29	–	–	CR	[16]
Myristic acid $\text{CH}_3(\text{CH}_2)_{12}\text{COOH}$	51.5	204.5	–	–	98%	[25]
	51.80	178.14	51.74	181.63	> 98%	[26]
	52.2	182.6	–	–	97%	[21]
	52.2	182.6	–	–	98%	[19]
	$52.44 \pm 0.11$	$210.70 \pm 1.65$	$52.49 \pm 0.14$	$212.65 \pm 1.96$	> 98%	[18]
	52.99	181.0	–	–	95%	[20]
	53.73	187.3	52.09	184.9	–	[23]
	53.8	192.0	–	–	95%	[8]
	54.7	178.79	–	–	CR	[16]
	58	186.6	–	–	–	[15]
	58	186.6	–	–	–	[27]
Palmitic acid $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	58.9	189.6	–	–	96%	[19,21]
	59.40	218.53	58.23	216.46	96%	[17]
	59.9	197.9	–	–	95%	[8]
	60.42	233.24	59.88	237.11	> 98%	[26]
	$60.45 \pm 0.14$	$221.42 \pm 1.65$	$59.88 \pm 0.12$	$226.56 \pm 1.87$	> 98%	[18]
	61	203.4	–	–	97%	[28]
	61.31	197.9	–	–	97%	[20]
	62.11	212.1	60.38	214.6	–	[23]
	62.4	208.0	–	–	98%	[29]
	63	212.1	–	–	CR	[14]
	64	185.4	–	–	–	[15]
	64.5	208.20	–	–	99.3%	[21]
	65.5	207	58.68	205.39	CR	[30]
Stearic acid $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	53.8	174.6	–	–	> 90%	[8]
	54.70	159.3	–	–	90%	[20]
	56.89	182.39	52.12	177.80	–	[31]
	58.22	180.56	–	–	CR	[16]
	59.9	177.84	54.7	185.68	CS	[32]
	66.82	258.98	66.36	263.32	> 98%	[26]
	$66.87 \pm 0.12$	$242.15 \pm 1.78$	$66.36 \pm 0.09$	$246.74 \pm 1.76$	> 98%	[18]
	67.8	198.9	–	–	97%	[21]
	68.8	198.8	–	–	–	[33]
	68.96	222.8	37.06	226.7	–	[23]
	69	202.5	–	–	–	[15]
	69.1	201.8	–	–	97%	[19]
	69.6	222.2	–	–	CR	[14]
	70.9	210.8	–	–	97%	[9]
Oleic acid $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	13.6	138.07	–	–	> 99.9%	[10]

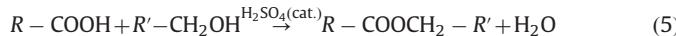
suitable to be applied in the heating system, water heating system, phase wall board, concrete, textiles with PCM and other engineering fields.

### 2.3. Fatty acid esters

Due to the high phase change temperature, a certain corrosivity, bad odor and sublimation during heating process of fatty acids,

some researchers replaced them with their derivative fatty acid esters which can be obtained via the esterification of fatty acids with alcohols. In the family of fatty acids, stearic acid (SA) and palmitic acid (PA) always have a high phase change temperature in many aspects of application, so in the reaction of esterification, researchers always choose SA and PA as acids, and short-chain or long-chain monohydric alcohols, dihydric alcohols and polyatomic alcohols with different carbon chain length as alcohols. A general

reaction for esterification is shown as Eq. (5).



Feldman et al. [38] prepared 12 kinds of short-chain monohydric alcohol stearate via the etherification of four kinds of mixed stearic acids with different purities with methyl alcohol, propyl alcohol and butyl alcohol respectively. With phase change temperature ranges and latent heat values of 54–57 °C and 180 J/g, 60–66 °C and 206 J/g, 65–68 °C and 209 J/g, and 51–56 °C and 180 J/g respectively, the four stearic acids showed melting temperature and freezing temperature ranges of 17–34 °C and 20–32 °C respectively. The latent heat of methyl stearate was 181–199 J/g, of propyl stearate is 156–178 J/g, and of butyl stearate was a lower 139–145 J/g. It can be seen that the latent heat of stearate decreased with the increase of alcohols' carbon chain length. Sari et al. [39] prepared butyl stearate and isopropyl stearate via Fischer esterification reaction with  $H_2SO_4$  as a catalyst. The DSC results show that butyl stearate and isopropyl stearate had melting temperatures of 23.67 °C and 22.12 °C

**Table 2**  
Density, specific heat and thermal conductivity of fatty acids as PCMs [15].

	Capric acid (CA)	Lauric acid (LA)	Myristic acid (MA)	Palmitic acid (PA)	Stearic acid (SA)
Density( $\text{kg/m}^3$ )					
Solid	1004	1007	990	989	965
Liquid	878	862	861	850	848
Specific heat ( $\text{kJ/kg K}$ )					
Solid	1.9	1.7	1.7	1.9	1.6
Liquid	2.1	2.3	2.4	2.8	2.2
Thermal conductivity Liquid ( $\text{W/m K}$ )					
	0.153	0.147	0.150	0.162	0.172

respectively and freezing temperatures of 24.45 °C and 21.99 °C respectively (the melting temperature and freezing temperature of SA were 68.86 °C and 68.91 °C respectively); and had melting latent heat of 121.0 J/g and 113.1 J/g respectively and freezing latent heat of 128.4 J/g and 113.1 J/g respectively (the melting and freezing latent heats of SA were 252.7 J/g and 254.1 J/g respectively). It can be seen from the phase change temperature of the above monohydric alcohol stearate that alcohols can effectively lower the phase change temperature of stearate, making it more applicable in low-temperature heat storage.

Aydin et al. [40] prepared a range of long-chain fatty acid esters via the etherification of myristyl alcohol with lauric, myristic, palmitic, stearic and arachidic acids under vacuum and in the absence of any catalyst. Those long-chain fatty acid esters showed a melting temperature range of 38–53 °C, and phase change enthalpy values of above 200 J/g. Compared with other PCMs with a phase change enthalpy of the same 200 J/g but a melting temperature of above 60 °C, those long-chain fatty acid esters feature the advantages of a better application at a low temperature and a lower degree of supercooling. With the same method, they also synthesized four long-chain fatty acid esters with myristyl alcohol and odd carbon atom fatty acids of 1-tridecanoic, 1-pentadecanoic, 1-heptadecanoic and 1-nonadecanoic acids as PCMs [41]. The fatty acid esters showed a phase change temperature range of 40–50 °C and a phase change enthalpy range of 203–218 J/g. Aydin et al. [42], using 1-hexadecanol and C10–C20 fatty acids with even carbon numbers as materials, prepared six kinds of 1-hexadecanol long-chain fatty acid ester low temperature PCMs with a phase change temperature range of 29–60 °C and a latent heat range of 186–226 J/g, which can be well applied in the micro and macro encapsulated exothermic condensed system.

Li et al. [43] prepared Butanediol di-stearate solid–liquid PCMs through the esterification of stearic acid with 1,4-butanediol. The

**Table 3**  
Properties of eutectic mixtures of fatty acids as PCMs.

Binary fatty acids	Proportion	Melting temperature (°C)	Melting enthalpy (J/g)	Freezing temperature (°C)	Freezing enthalpy (J/g)	Purity	Reference
CA:LA	61.5:38.5	19.1	–	–	–	–	[14]
	67:33	22.81	154.16	–	–	CR:CR	[16]
	65.12:34.88	19.67	126.562	–	–	CR:CR	[13]
	64:36	19.62	149.95	19.41	148.99	98%:98%	[34]
CA:MA	72:28	25.36	139.2	–	–	CR:CR	[16]
	74:26	22.16	154.83	21.18	156.42	98%:97%	[35]
CA:PA	75.2:24.8	22.1	–	–	–	–	[14]
	76.5:23.5	21.85	171.22	22.15	173.16	98%:97%	[17]
	76.5:23.5	23.12	156.44	22.15	150.29	98%:98%	[34]
CA:SA	86.6:13.4	26.8	–	–	–	–	[14]
	77:23	27.78	122.58	–	–	CR:CR	[16]
	83:17	25.39	188.15	25.2	184.11	98%:97%	[34]
LA:MA	58:42	35.18	162.27	–	–	CR:CR	[16]
	61.27:38.73	33.27	173.6	33.71	168.0	–	[23]
	66:34	34.2	166.8	–	–	98%:97%	[21]
LA:PA	69:31	35.2	–	–	–	–	[14]
	69:31	35.2	166.3	–	–	98%:96%	[21]
	77.51:22.49	33.60	169.6	31.22	168.3	–	[23]
LA:SA	75.5:24.5	36.7	–	–	–	–	[14]
	75.5:24.5	37	182.7	–	–	98%:97%	[19]
MA:PA	58:42	42.6	169.7	–	–	97%:96%	[19]
	66.92:33.08	45.36	183.1	43.80	185.6	–	[23]
MA:SA	64:36	44.1	182.4	–	–	97%:97%	[21]
	77.42:22.58	46.41	180.6	42.09	177.3	–	[23]
PA:SA	62.99:37.01	53.69	204.7	53.45	204.2	–	[23]
	64.2:35.8	53.2	–	–	–	–	[14]
	64.2:35.8	52.3	181.7	–	–	96%:97%	[19]

DSC test results show that the phase change temperature of Butanediol di-stearate was 41.80 °C, and the latent heat was 181.97 J/g. Due to SA with a phase change temperature range of 63–69.9 °C, it is more favorable to be applied in thermal energy storage at a low temperature. Li et al. [44] also made further preparation of a range of dihydric alcohol stearates as PCMs (dihydric alcohol includes 1,2-ethanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol and 1,10-decanediol). According to DSC analysis, as the number of carbon atoms increased from 2 to 10, the phase change temperatures of these dihydric alcohol stearates were 54.4, 46.5, 38.5, 41.4 and 49.8 °C respectively, and the latent heats were 189, 181, 164, 156 and 134 J/g respectively. The change of phase change temperature is caused by the crystal structure and crystallinity of materials.

Sari et al. prepared a series of solid–liquid fatty acid esters as PCMs with glycerol [39,45] containing three hydroxyl radicals, erythritol [46] containing four hydroxyl radicals, xylitol [47] containing five hydroxyl radicals, galactitol [48] containing six hydroxyl radicals and mannitol [49] containing six hydroxyl radicals as raw materials respectively in different reaction conditions. Compared with polyalcohol materials with high phase change temperature and latent heat, and a very high degree of supercooling, fatty acid esters as PCMs feature a proper phase change temperature, a higher latent heat, a lower degree of supercooling, and a higher thermal reliability which make them more suitable to be applied to low temperature phase change energy storage. Through the TG method, their thermal stability was tested. Besides, their thermal conductivity was increased by adding a certain amount of expanded graphite to improve the rate of thermal storage and release, so as to apply them to thermal storage, buildings, solar energy storage and other fields more effectively.

On the whole, compared with fatty acids, fatty acid esters obtained through the etherification of fatty acids with alcohols have a lower phase change temperature, so they can be applied to thermal energy storage at a low temperature more effectively. The effect of alcohols on the thermal properties of fatty acid esters is relatively great.

#### 2.4. Other mixtures of fatty acids

The phase change temperature and latent heat of fatty acids derivatives as PCMs can be adjusted by several ways. According to the above, fatty acid eutectic mixtures and fatty acids esters are two usual methods to adjust the phase change temperature of fatty acids. And it is also can be achieved by the mixtures with fatty alcohols or poly(ethylene oxide) (PEO), and form binary and ternary mixed PCMs with oleic acid, pentadecane and other substances with a low melting temperature.

Zuo et al. [50,22] prepared the eutectic mixtures of caprylic acid/1-dodecanol and lauric acid/1-tetradecanol respectively. Regarding the eutectic mixture of caprylic acid/1-dodecanol, the melting temperature was 6.52 °C, the latent heat was 171.06 J/g, and the content of caprylic acid was 70 wt% when the temperature reached the eutectic point. Regarding the mixture of lauric acid/1-tetradecanol, the eutectic temperature was 24.33 °C, the latent heat was 161.45 J/g, and the mass fraction of LA was 40%.

Pielichowska et al. [51,52] prepared a series of poly(ethylene oxide)/stearic acid (PEO/SA) and poly(ethylene oxide)/lauric acid (PEO/LA) mixtures by cooling down melted mixed PEO/SA and PEO/LA at different mass ratios. In PEO/SA system, the mixtures had a eutectic point when the mass ratio of PEO to SA was 8:2, but no common phase change temperature appeared during the process of freezing, for PEO has a relatively high degree of supercooling that makes the mixture of it and SA have different phase changes during melt and freeze. In PEO/SA system, when the mass ratio of PEO to LA was 1:1, the latent heat of melting and of

freezing reached the maximum values of 208.3 J/g and 202.0 J/g respectively. Pielichowska et al. [53] did further research into the structure, form and hydrogen bonding between components of PEO/SA and PEO/LA mixtures through a range of characterization techniques, and explained the reason why the measured phase change enthalpy of mixtures is larger than the theoretical value.

Cedeno et al. [9] made use of DSC to do research into the melting process of three kinds of fatty acids (palmitic acid, stearic acid and oleic) and their binary and ternary mixtures. Since oleic would go through two phase changes (solid–solid, solid–liquid) during the temperature-rise period and temperature-fall period from –100 °C to 100 °C, the melting process curves of the binary and ternary mixtures of it and PA and SA had two endothermic peaks. With the increase of the content of oleic, the solid–liquid phase change temperature of the binary mixtures of Oleic and PA, and of oleic and SA decreased, and the melting heat had no significant change. The eutectic temperature of the eutectic mixtures of PA and SA was 331 K. The melting heat of ternary mixtures linearly reduced as the content of oleic increased.

Dimaano et al. [54] mixed capric–lauric acid (CA–LA) (65 mol %:35 mol%) whose melting temperature was 18 °C and pentadecane (P) whose melting temperature was 9.9 °C in different proportions (CA–LA:P=90:10, 70:30, 50:50 by volume) firstly, and the DSC test results show that the melting curve of the mixture of CA–LA and P in proportion of 90:10 had one melting peak only, indicating that the mixture in such a proportion had good uniformity, and melting temperature ranged from 9.4 to 21.8 °C. Results of the research show that among the mixtures of CA–LA and P, the mixture with a mass ratio of 50:50 had the largest heat storage volume, but the two obvious melting peaks indicated that mixture had a certain heterogeneity. Comparing with the mixture of CA–LA and P with a mass ratio of 50:50, the mixture of CA–LA and P with a mass ratio of 90:10 had a wider melting range; compared with pure CA–LA, the mixture of CA–LA and P with a mass ratio of 90:10 can provide a larger heat storage capacity, which can improve the melting properties of pure CA–LA. Dimaano et al. [55] did further research into the practice of improving the thermal properties and lowering the melting temperature of CA–LA acid by adding 10 mol% low melting temperature substances of methyl salicylate, eugenol and cineole into CA–LA (65 mol%:35 mol%) whose melting temperature was 18 °C, so as to make it more applicable in cooling application. According to DSC test results, the melting temperatures of CA–LA+methyl salicylate, CA–LA+cineole and CA–LA+eugenol were 12.5, 12.3 and 13.9 °C respectively.

#### 2.5. Thermal reliability of fatty acids

The thermal reliability of PCMs is an important index to test whether they can be applied in practical engineering. Researchers usually use the accelerated cycling test and DSC test to compare the phase-change temperature and latent heat of the fatty acids as PCMs after multiple cycling, so as to analyze their thermal reliability. In a typical accelerated cycling test, a certain amount of fatty acids was added into a cylindrical airtight container, then melted and cooled down with the help of thermostatic instruments. After different cycles, a small amount of samples was weighted for the DSC test.

Sari [20] studied the thermal reliability of four pure fatty acids of lauric acid (LA), myristic (MA), palmitic acid (PA) and stearic acid (SA) (purity%: 97, 95, 96 and 90) through the accelerated cycling test and DSC test. The DSC test results show that the melting temperature of the fatty acids as PCMs decreased as the number of cycles increased and its variation range was 0.07–7.87 °C. Compared with the change of the melting temperature, the change of the latent heat of the PCMs was not obvious, and most of the latent heat change rates were between –1.0% and

27.7%. The paper believes that the changing relationship between the latent heat and thermo-cycling is caused by the purity of the materials but does not give any introduction to the specific influence mechanism. Sari et al. [8] also studied the thermal reliability of SA, PA, MA and LA with industrial purity (90–95%). Through 910 thermal cycles, the DSC test results show that the latent heat of SA, PA, MA and LA decreased by 31.9%, 17.8%, 17.1% and 37.2% respectively while there was no significant change of their phase change temperatures. Sharma et al. [56] studied the change of the melting latent heat and temperature of acetamide, stearic acid and paraffin wax, which are industrial PCMs, through a 1500-cycle accelerated cycling test, and the purity of the PCMs was between 95% and 98%. The test results show that, although there may have been influence of the water which was absorbed by acetamide in the environment, there was no significant change in the melting temperature and latent heat. The stearic acid melted at a very wide temperature range and its melting temperature was unstable. Its latent heat decreased by 20.65% after 1500 cycles, and the latent heat of the paraffin wax also decreased by 28%. The decrease of the latent heat of SA and paraffin wax was caused by the impurities in them. The research results show that before using industrial PCMs, the thermal cycling test is more important.

Sari et al. [19,21,57,58] adopted the thermal cycling test to analyze the thermal reliability of such eutectic mixtures as lauric-stearic acid (LA-SA), myrisitic-palmitic acid (MA-PA), palmitic-stearic acid (PA-SA), lauric-myristic acid (LA-MA), lauric-palmitic acid (LA-PA), myrisitic-stearic acid (MA-SA) and capric-palmitic acid (CA-PA). According to the literature [19], three eutectic mixtures were subject to 360 thermal cycles at most. The melting temperature had a variation of  $-0.44^{\circ}\text{C}$  after 90 cycles and  $0.36^{\circ}\text{C}$  after 360 cycles for LA-SA eutectic mixture; of  $-0.56^{\circ}\text{C}$  after 90 cycles and  $-0.2^{\circ}\text{C}$  after 360 cycles for MA-PA eutectic mixture; and of  $1.13^{\circ}\text{C}$  after 90 cycles and  $1.28^{\circ}\text{C}$  after 360 cycles for PA-SA eutectic mixture. After 90 cycles, the latent heat of fusion,  $\Delta H_{\text{fus}}$ , had a variation of  $-6.2\%$  for LA-SA,  $-7.2\%$  for MA-PA and  $2.2\%$  for PA-SA eutectic mixtures; and after 360 cycles, of  $0.2\%$  for LA-SA,  $2.9\%$  for MA-PA and  $2.5\%$  for PA-SA eutectic mixtures. In literature [57,21], LA-MA, LA-PA and MA-SA eutectic mixtures were subject to 1460 melting/freezing cycles. After 720 cycles, the temperature had a variation of  $0.15^{\circ}\text{C}$  for LA-MA,  $-0.18^{\circ}\text{C}$  for LA-PA and  $-0.98^{\circ}\text{C}$  for MA-SA eutectic mixtures, and after 1460 cycles, the variations were  $-0.30^{\circ}\text{C}$  for LA-MA,  $-0.40^{\circ}\text{C}$  for LA-PA and  $-1.11^{\circ}\text{C}$  for MA-SA eutectic mixtures. As for the change of latent heat, after 720 cycles, the variations were  $0.3\%$  for LA-MA,  $1.7\%$  for LA-PA and  $0.8\%$  for MA-SA eutectic mixtures, and after 1460 cycles, the variations were  $2.4\%$  for LA-MA,  $1.5\%$  for LA-PA and  $1.0\%$  for MA-SA eutectic mixtures. According to the change in the melting temperature of PCMs in the thermal cycling process, it is difficult to find a relationship between the change of melting temperature and the number of thermal cycling. The change of the latent heat of eutectic mixtures, which is caused by the purity of the materials, was not significant and had no law. In literature [58], CA-PA was subject to as high as 5000 accelerated thermal cycles. The results show there was no significant change in either its phase change temperature or latent heat, which indicates that CA-PA eutectic mixture has excellent long-time thermal reliability.

Aydin et al. [40] found in the thermal reliability study of even carbon atom long-chain fatty acid esters as PCMs that after 1000 thermal cycling, the changes of the phase change temperature and enthalpy were less than 1% and no such phenomena as phase separation or decomposition happened. TGA research results show the temperature at which the PCMs began to decompose and the temperature at which their weight lost 5 wt% were higher than  $270^{\circ}\text{C}$  and  $240^{\circ}\text{C}$  respectively and the reliability of the fatty acids increased as the number of the carbon atoms of the fatty acids increased, which shows that the PCMs can endure the

**Table 4**

Thermal properties of the fatty acids, polyalcohol and fatty acids esters before and after thermal cycling.

PCMs	Thermal energy storage properties			
	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H_m$ (J/g)	$T_f$ ( $^{\circ}\text{C}$ )	$\Delta H_f$ (J/g)
MA	54.37	197.4	51.45	200.9
PA	62.74	214.4	58.82	208.0
SA	68.86	252.7	68.91	254.1
Glycerol trimyristate (GTM) [45]	31.96	154.3	31.62	1448.8
GTM (after1000 cycle)	31.22	151.8	30.91	153.4
Glycerol tripalmitate (GTP)	58.50	185.9	54.83	182.9
GTP(after1000 cycle)	57.45	175.8	54.46	177.8
Glycerol tristearate (GTS)	63.45	149.4	64.58	151.7
GTS(after1000 cycle)	62.83	152.8	60.06	147.5
Erythritol [46]	118.4	379.57	36.22	255.95
Erythritol tetrapalmitate (ETP)	21.93	201.10	18.79	200.75
ETP(after1000 cycle)	20.88	200.37	17.06	187.71
Erythritol tetrastearate (ETS)	30.35	208.84	28.79	207.16
ETS(after 1000 cycle)	33.35	207.81	27.84	205.16
Xylitol [47]	93.20	–	–	–
Xylitol pentapalmitate (XPP)	18.75	170.05	–	–
XPP(after 1000 cycle)	18.35	164.77	–	–
Xylitol pentastearate (XPS)	32.35	205.65	–	–
XPS(after 1000 cycle)	31.04	197.25	–	–
Galactitol[48]	187.41	401.76	115.78	285.18
Galactitol hexa palmitate (GHP)	31.78	201.66	30.02	197.14
GHP(after 1000 cycle)	30.93	200.70	28.69	196.87
Galactitol hexa stearate (GHS)	47.79	251.05	45.19	233.49
GHS(after 1000 cycle)	49.46	206.48	48.90	207.55

encapsulation process under about  $180^{\circ}\text{C}$  without decomposition. All in all, long chain fatty acids as PCMs are promising low-temperature heat storage materials.

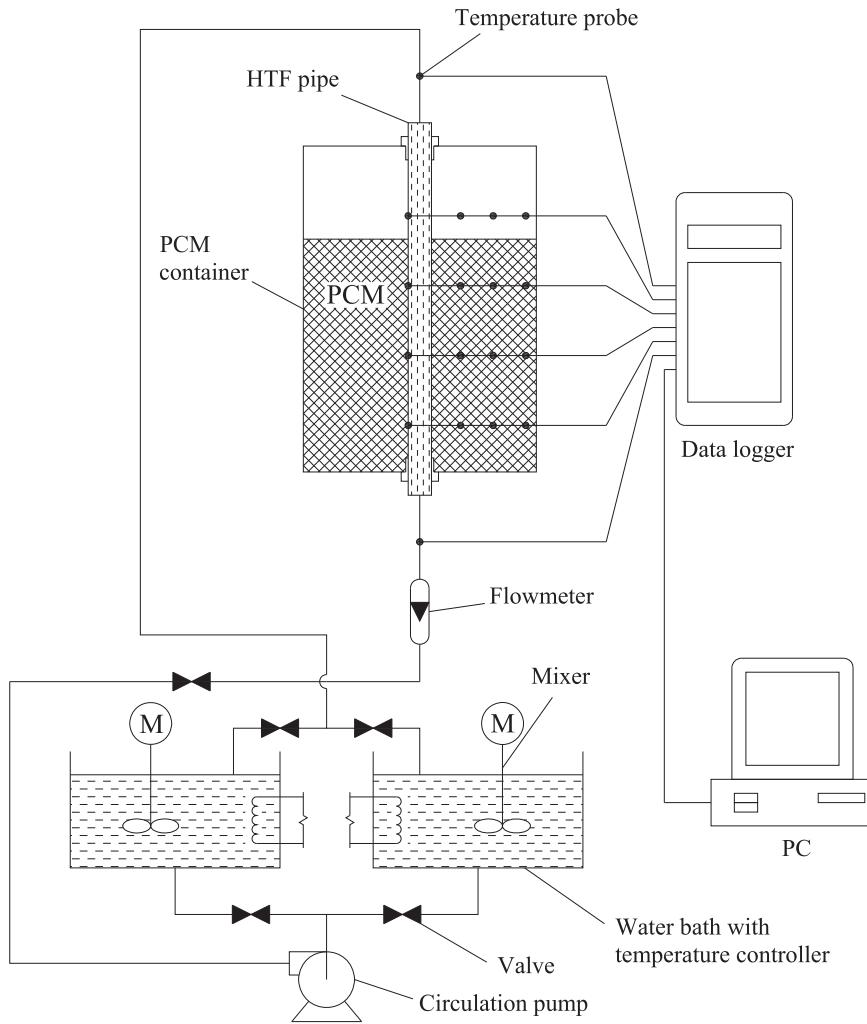
In literature [39], Butyl stearate, Isopropyl stearate and Glycerol tristearate were subject to 1000 thermal cycles for DSC test to study their thermal reliabilities, through which, it is found that their melting temperature and freezing temperatures ranges were  $0.62\text{--}0.77^{\circ}\text{C}$  and  $0.12\text{--}4.52^{\circ}\text{C}$  respectively and the melting and latent heat of the three PCMs changed by  $2.8\%$ ,  $-4.6\%$  and  $2.3\%$  and  $-2.2\%$ ,  $0.9\%$  and  $-2.8\%$ . In literature [45–48], the changes of the phase change temperature and latent heat of the fatty acids before and after 1000 thermal cycles are shown in Table 4 below.

From the research above we can see that, on the whole, fatty acids as PCMs have good thermal reliability and the changes in the phase change temperature and latent heat are not significant (especially the change in latent heat) and the main reason causing the change is impurities.

## 2.6. Heat transfer characteristics of fatty acids in a thermal energy storage unit

In the engineering application, fatty acids as PCMs may be encapsulated in a thermal energy storage unit. It is necessary to study the heat transfer characteristics of fatty acids in the unit.

Using the ring cavity of the concentric circular tube as the phase change unit to study the heat transfer characteristics of fatty acids as PCMs in a unit is a common method, and the schematic diagram of the experimental setup is shown in Fig. 1. Sari et al. [25,28,59] studied the thermal properties and phase change stability of MA, PA and SA as PCMs through experiments. The PCMs were filled in the ring cavities of two concentric circular tubes and cool and hot water was used to heat and cool the PCMs. The experimental results show that the melting stability of the PCMs was better in the radial direction than that in the axial direction. In the melting process, the heat convection in the liquid phase played an important role while the flow velocity of the heat transfer liquid and the inlet temperature had no significant impact on the phase change of the fatty acids. When the heat transfer



**Fig. 1.** Experimental setup of fatty acids in a thermal energy storage unit.

tube was placed horizontally, the heat transfer efficiency was higher and the phase change property, more stable than that when the tube was placed vertically. The average heat storage efficiency of the MA in the PCM tube was 54%, that of SA, 50.3%, and that of PA, 53.3%, which indicates that nearly half of the energy was not stored. Sari [60] took LA as a PCM and studied the influence of heat transfer fluid (HTF) Reynolds and Stefan number as the inlet conditions on phase change parameters and calculated the coefficient of heat transfer and heat flow. The research results show that Reynolds and Stefan number have a greater impact on the average coefficient of heat transfer and heat flow in the melting process than that in the condensing process. Sari et al. [61–66], on the basis of preparing a series of eutectic mixtures, studied the thermal properties of MA-SA, LA-MA, LA-SA, PA-SA, MA-PA and LA-PA eutectic mixtures in a unit respectively. The results show that the thermal properties of eutectic mixtures in the phase change process are basically the same with those of elementary fatty acid substances.

Numerical calculation is also one of the methods used to study the thermal properties of fatty acids as PCMs in a unit. Sharma et al. [15] studied the latent heat storage property of fatty acids in heat exchangers made of different materials through numerical simulation. He selected CA, LA, MA, PA and SA as PCMs and calculated the melting fraction via the enthalpy-method-based two-dimension simulation model. The calculation results show that CA had excellent adaptability in the latent heat storage system and the thermal conductivity of the heat exchanger had little effect on the melting

fraction. Wu et al. [27] also adopted the numerical simulation method and studied the dynamic property of the packed bed solar energy storage system with MA as a PCM. The water was taken as the heat transfer flow, and MA was sealed in a high-density polyethylene ball with an outer diameter of 50 mm and a thickness of 1 mm. They set up a numerical calculation model on the basis of the energy balance of HTF and PCM. The temperatures of the PCM and HTF, solid fraction and heat release rate during the freezing process were calculated. To make the calculation easier, the following assumptions were made for the numerical calculation model: (1) the thermo-physical properties of PCM and HTF are temperature independent, (2) the effect of natural convection is neglected, (3) the velocity of HTF is large enough and velocity is regarded as fully developed flow in axial direction, and (4) heat loss from the packed bed to the surroundings is neglected.

Liu et al. [67,68] studied the thermal properties of stearic acids in the vertical ring unit during the freezing and melting process, analyzed the movement of the radial solid–liquid interface and the influence of Reynolds number on the heat transfer, and also made a simplified calculation on the heat flow. The results show that the new fin can enhance both the conduction and the natural convection heat transfer of PCMs, and the enhancement factor during freeze was estimated to be as high as 250%. The experimental results show that the enhancement mechanism of the fin was attributed to its ability to improve both heat conduction and natural convection very effectively. The influences of the fin size and pitch on the enhancement were also studied.

Veerappan et al. [69] first presented an analytical model based upon the quasi steady approximations for the melt and freeze of PCMs in a spherical container under isothermal boundary conditions at the external surface of the spherical shell. Considering the calculation models of the conduction, convection and heat generation of the spherical structure, the calculation results were closer to the experimental data. They also, with an analytical model, analyzed the phase change properties of PCMs including CA-LA (65–35 mol%), calcium chloride hexahydrate, *n*-octadecane and *n*-hexadecane and *n*-eicosane sealed in the spherical structure. The influence of the size of encapsulation, initial temperature of the PCMs, the external fluid temperature on freezing and melting mass fraction, and the total phase change time were also investigated. The analysis and calculation results of the five PCMs including CA-LA (65–35 mol%) and calcium chloride hexahydrate and so on show that  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  as a solar energy latent heat storage material has even better performance.

### 3. Fatty acid composites as PCMs

There are mainly two reasons for preparing fatty acids composites as PCMs. One is to enhance the heat conduction ability of PCMs to make good the defect that fatty acids as PCMs have poor heat conduction ability; and the other is to realize the stable form and solidification of PCMs. There are four preparation methods to stabilize PCMs: (1) adsorption; (2) polymer blends; (3) electrostatic spinning; and (4) microencapsulation. There are many advantages to make fatty acids into form-stable PCMs, including no need for additional encapsulation, cost-effectiveness, stable shape, and readiness for applications with tunable dimension.

#### 3.1. Composite PCMs with enhanced heat-conduction property

Fatty acids as PCMs have small thermal conductivity, which slows down the storage and heat release rate during the melting and solidification process. The currently used materials with excellent heat conduction property include carbon nanotubes (CNTs), carbon fiber, expanded graphite (EG), activated carbon, silica fume (SF) and activated montmorillonite (a-MMT) and so on.

Wang [70,29] composed multi-walled carbon nanotubes (MWCNTs) with palmitic acid. The average diameter, average length, and specific surface area of MWCNTs were 30 nm, 50 nm,  $60\text{ m}^2/\text{g}$  and PA 98% respectively. He first modified MWCNTs with the four modifying methods, namely acid oxidation (A-MWCNTs), mechanochemical reaction (M-MWCNTs), ball milling (B-MWCNTs) and grafting following acid oxidation (G-MWCNTs) and then added it into melted PA for ultrasonic processing, through which he obtained MWCNTs/PA composite PCMs with even dispersion. The test results show that when MWCNTs/PA increased to 1 wt%, the thermal conductivity of the M-MWCNTs/PA composite PCM was the highest and under 25 °C, the purer PA increased by 51.6%. As the content of MWCNTs/PA increased, the latent heat of the composite PCM decreased. When it increased to 1% (wt), the latent heat decreased to 184.0 J/g. Wang [71] also conducted comparative study on the change in the phase change temperature, latent heat and thermal conductivity of CNTs/PA composite PCM after grafting Oleylamine (G18) and octanol (G8) with the grafting following acid oxidation method. The phase change temperature of the PA-based composite PCM had no change compared to that of PA, while its latent heat decreased, which may be caused by the hydrogen bond between CNTs and the –COOH of PA. The CNTs/PA composite PCMs by grafting CNTs with G8 had higher thermal conductivity. Ji et al. [72] also added MWCNTs with a lot of oxygen-containing groups on the surface into PA. The hydrogen-bond interaction between MWCNTs and PA molecules made MWCNTs disperse evenly in the PA matrix,

which thus greatly increased the thermal conductivity of the composite PCM.

Adding carbon fiber (CF), expanded graphite (EG) can also increase the thermal conductivity of fatty acids as PCMs. Karaipekli et al. [33] studied the improvement of EG and carbon fiber CF on SA thermal properties. They added EG and CF with different mass fractions (2%, 4%, 7%, and 10%) into melted SA. As GE has more excellent compatibility in physical and chemical properties, the dispersity of SA in it is better than that in CF. The research results show that the thermal conductivity of the composite PCMs increased with the increase of EG and CF, in a linear relation. When the mass fractions of EG and FC increased to 10% respectively, the thermal conductivity of the composite PCMs increased by 279.3% and 217.2% respectively. The latent heats of pure SA, SA/EG (90/10 wt%) and SA/CF (90/10 wt%) were 198.8 J/g, 183.3 J/g and 184.6 J/g respectively. The latent heats of SA/EG and SA/CF only decreased by 8% and 7% compared with that of the pure PA, which indicates that the thermal conductivity of composite PCMs can be increased by adding EG and CF and that will not reduce much latent heat storage capacity. Sari et al. [73] made use of the porous structure and good heat conduction property of EG to prepare PA/EG composite PCM with a higher thermal conductivity. When the content of EG was 20 wt%, PA/EG composite PCM had no leakage under PA molten condition, but the thermal conductivity ( $0.6\text{ W}/(\text{m}\cdot\text{K})$ ) was 2.5 times higher than that of PA ( $0.17\text{ W}/(\text{m}\cdot\text{K})$ ). Zhang et al. [74] prepared LA-MA-PA ternary eutectic mixture with a phase change temperature of 31.41 °C at first, then synthesized LA-AM-PA/EG composite PCM (LA-MA-PA content: 94.7 wt%) with the LA-MA-PA prepared and EG by making use of the absorption of PCMs in EG. The heat conductivity of the LA-AM-PA/EG was much higher than that of the LA-MA-PA.

Fang et al. [31] mixed SA and EG with different mass ratios (1:1, 3:1 and 5:1) into 500 ml breaker and gave a 500 rpm magnetic stirring for 40 min at a constant temperature of 70 °C, and finally dried it for 3 h at 60 °C to prepare SA/EG composite PCM. The Fourier transform infrared (FT-IR) characterization test results show that there was no chemical reaction between SA and EG, and SA only existed in pore of EG via capillary effect and surface tension. X-ray diffractometer (XRD) results show that the grain size of EG became small due to the limitation of SA crystal in the composite PCM. Scanning electron microscopy (SEM) characterization test results show that SA was uniformly distributed in the composite PCM. When the composite PCM was in the molten state, there was no leakage of SA even though its maximum mass ratio was 83%. The thermal properties results of SA and the composite PCM in DSC test showed that the latent heat of the composite PCM increased as the increase of SA. As shown in Table 5, the research results show that the thermal diffusivity of the composite PCM increased as the increase of EG, and CPCM3 (see Table 5) with a PA content of 83 wt% was improved by 10 times compared to that of pure PA. Furthermore, thermogravimetric analysis (TGA) proved that the composite PCM had a good thermal stability.

Chen et al. [23] also took activated carbon (AC) with high thermal conductivity as a setting material to prepare LA/AC

**Table 5**  
Thermal diffusivities of SA and EG compositeS as a PCM [31].

Sample name	SA and EG mass ratio	Thermal diffusivity ( $\text{mm}^2/\text{s}$ )	Improvement times
CPCM1	1:1	4.88	43.36
CPCM2	3:1	2.53	22.00
CPCM3	5:1	1.24	10.27
SA	1:0	0.11	0

composite PCMs with different mass ratios (1:5, 1:4, 1:3, 1:2). FT-IR, XRD and SEM comprehensive characterization test results show that LA was combined with porous medium AC via capillary and surface tension, and AC had a maximum absorption rate of 33.3 wt % in LA. The addition of 1 wt% EG in the composite PCM whose LA/AC mass ratio was 1:2 can make the thermal conductivity of the composite PCM respectively increase by 46.7% and 71.1% under solid state (25 °C) and molten state (50 °C). DSC test results show that the temperature and latent heat of the composite PCMs slightly increased as the increase of LA, and the composite PCM with LA content of 33.3 wt% had a melting temperature and enthalpy of 44.07 °C and 65.14 J/g respectively, and a freezing temperature and enthalpy of 42.83 °C and 62.96 J/g respectively. TGA results show that AC can improve the thermal stability of composite PCMs.

Wang et al. [32,75] prepared form-stable composite PCMs SA/SF and MA-SA/a-MMT with silica fume (SF) and activated montmorillonite (a-MMT) as supporting materials and stearic acid (SA) as PCMs, and then verified the leakage of the composite PCMs by using the method of vacuum drying at 80 °C for 24 h. By means of SEM and FT-IR tests, they carried out a research on the micro results and composite way of the composite PCMs, and found that SA settled on the surface of form-stable materials via the hydrogen bond forming between SF and a-MMT. DSC test results show that the phase change temperature of the composite PCMs changed a little compared to that of SA. FT-IR test results show that there was no chemical reaction between SA and SF, a-MMT, the change of SA/SF melting and freezing latent heat were –0.69 and –0.33 J/g respectively, and the melting and freezing latent heat of SA/a-MMT changed by –0.59% and –1.01% respectively. The heat storage and release speed of composite PCMs were greatly improved due to the fact that SF and a-MMT has relatively high thermal conductivity.

### 3.2. Form-stable composite PCMs

#### 3.2.1. PCMs prepared in porous matrix by absorption

By use of the porous medium as a matrix, form-stable PCMs can be prepared by virtue of the absorption of fatty acids in the pore structure. Porous medium materials are well compatible with base materials, which is better for the application of PCMs in the energy storage system.

Sarı et al. [76,77] used expanded perlite (EP) as supporting material and CA and LA as PCM to prepare CA/EP and LA/EP composite PCMs. It is found that LA was well compatible with EP, and EP had a maximum absorption ratio of 55 wt% on CA and 60 wt% on LA. DSC test results show that CA had melting and freezing temperatures of 32.14 °C and 32.53 °C respectively, and latent heat of melting and freezing values of 156.40 J/g and 154.24 J/g respectively; while CA/EP had melting and freezing temperatures and latent heat of 31.80 and 31.61 °C and 158.73 and 164.65 J/g respectively. For LA, it had melting and freezing temperatures of 44.15 °C and 41.48 °C respectively, and latent heat of melting and freezing values of 158.73 J/g and 164.65 J/g respectively; while LA/EP had melting and freezing temperatures and latent heat of 44.13 and 40.97 °C and 93.36 and 94.87 J/g respectively. Only little change happened on the phase change temperature and phase change enthalpy of CA/EP after 5000 thermal cycles and LA/EP after 1000 thermal cycles. In order to enhance the thermal conductivity of the composite PCMs, the authors creased the thermal conductivity of CA/EP and LA/EP by 64% and 86% respectively by adding 10 wt% EG.

Mei et al. [12] prepared the CA/halloysite nanotube (HNT) form-stable composite PCM by using the ultrasonic wave radiating method. TEM and FT-IR characterization tests results showed that the hydrogen bond structure between HNT and CA made the composite PCM a better absorption to CA, and there was no

chemical reaction between HNT and CA. The composite PCM had a maximum absorption ratio of 60 wt% on CA, without any leakage even after 50 melting and freezing cycles. The melting temperature and latent heat of composite PCM CA/HNT were 29.34 °C and 75.52 J/g respectively, and the freezing temperature and latent heat were 25.28 °C and 75.81 J/g respectively. (The melting temperature and latent heat of CA is 29.62 °C and 139.77 J/g respectively, and the freezing temperature and latent heat is 25.57 °C and 140.12 J/g respectively). After 5 wt% graphite was added, the energy storage and release speed of the composite PCM increased by 1.8 and 1.7 times respectively. It was tested that the thermal conductivity of composite PCM CA/HNT/G was 0.758 W/m K, increased by 58% compared to 0.479 W/m K of that of CA/HNT.

Karaipeki et al. [35,78] selected expanded perlite (EP) and vermiculite (VMT) as supporting materials and the eutectic mixture of capric acid and myristic acid (CA-MA) as PCMs to prepare CA-MA/EP and CA-MA/VMT form-stable composite PCMs by vacuum impregnation method. The SEM and FT-IR characterization test results showed the micromorphology and structure of the composite PCMs, and proved that the eutectic mixture of fatty acids had a good physical compatibility with porous materials. CA-MA/EP composite PCM had a maximum CA-MA content of 55 wt%, and CA-MA/VMT had a maximum absorption ratio of 20 wt% on CA-MA. DSC test results show that the melting and freezing temperatures and enthalpy values of CA-MA eutectic mixture were 22.61, 21.18 °C and 154.83, 156.42 J/g; the melting and freezing temperature and enthalpy values of CA-MA/EP composite PCM were 21.70, 20.70 °C and 85.40, 89.75 J/g; the melting and freezing temperature and enthalpy values of CA-MA/VMT composite PCM were 19.75 °C, 17.05 °C and 27.46 J/g, 31.42 J/g. It can be seen that VMT has a low absorption ratio on CA-MA and it is unable to effectively improve heat storage capacity of composite PCMs; therefore, Karaipekli [34] made an expansion treatment on vermiculite, and as a result, the absorption ratio of expanded vermiculite on the eutectic mixtures fatty acids was increased to 40 wt%, thus the enthalpy of composite PCMs was increased accordingly. The research also shows that there was no chemical change in the composite PCMs after 5000 thermal cycling, and small changes happened in their phase change temperature and enthalpy. 10 wt% EP was added to increase the thermal conductivity of the composite PCMs. The thermal conductivity of VWT is 0.065 W/m K, while the thermal conductivity of CA-LA/VMT, CA-PA/VMT and CA-SA/VMT were tested as 0.18 W/m K, 0.20 W/m K and 0.23 W/m K. By such a way, the heat storage and release speed of form-stable PCMs can be increased.

Li et al. [14,79] utilized diatomite as supporting material and CA-LA eutectic mixture as PCM to prepare form-stable composite PCMs. The diatomite has a maximum absorption rate of 66% on CA-LA. The phase change temperature and latent heat of CA-LA eutectic mixture are 16.36 °C and 117.12 J/g respectively; however, the phase change temperature and latent heat of CA-LA/diatomite were tested as 16.74 °C and 66.81 J/g respectively. Compared to the eutectic mixture of fatty acids, the composite PCM changed a little in phase change temperature, which will not affect its application. After 50 melting/freezing cycles of the composite PCM, it was found that the phase change temperature only decreased by 0.1 °C, indicating a good thermal reliability. Li et al. [80] also utilized attapulgite (A) as a supporting material, and CA-PA eutectic mixture as a phase change material to prepare CA-PA/A composite PCM by using the vacuum method. The maximum amount of CA-PA in CA-PA/A composite PCM was 35 wt%. DSC test results show that the phase change temperatures of CA-PA and CA-PA/A were 21.80 °C and 21.71 °C respectively, and their latent heats were 138.4 J/g and 48.2 J/g respectively.

Karaipekli et al. [81,82] prepared a series of form-stable composite PCMs by using cement, gypsum, diatomite and expanded

perlite (EP) as supporting materials, and Erythritol tetra palmitate (ETP) and Erythritol tetra stearate (ETS) as PCMs by the direct immersion method. It was found that via SEM and FT-IR tests that ETP and ETS were distributed in mesh pore structure of the setting materials via capillary effect and surface tension. The fatty acid ester had a maximum content of 18 wt% for ester/cement composite, 22 wt% for ester/gypsum composite, 57 wt% for ester/diatomite composite and 62 wt% for ester/EP composite respectively. DSC test results show that the melting temperature of the composite PCMs increased when the fatty acid esters were added into gypsum and cement, and decreased when the fatty acid esters were added into diatomite and EP; and the freezing temperature of the composite PCMs decreased when ETP was added to the setting materials, and increased when EPS was added into the setting materials. As the absorption ratio of setting materials on fatty acid esters increased, the latent heat of the composite PCMs also increased. The thermal prosperity test results show that after 1000 thermal cycles, that the composite PCMs tended to have a good thermal reliability.

Sari et al. [83] chose cement, gypsum, diatomite, perlite and vermiculite as supporting materials, and xylitol penta palmitate (XPP) and xylitol penta stearate (XPS) esters as PCMs to prepare form-stable composite PCMs. Their absorption ratio on XPP and XPS were 22, 17, 67, 48 and 42 wt% respectively. DSC test results show that the melting phase change temperature range and latent heat of melting range of the composite PCMs were 20–35 °C and 38–126 J/g; TG test results show that the composite PCMs had excellent thermal stability within its work temperature range. The thermal cycle test reflects that the composite PCMs had good thermal reliability and chemical reliability. Sari et al. [84] also took galactitol hexa myristate (GHM) and galactitol hexa laurate (GHL) esters as PCMs, and perlite, diatomite and vermiculite of porous mesh structure as setting materials to prepare form-stable composite PCMs. GHM's contents in three kinds of setting materials were 67, 55 and 52 wt% respectively, and GHL's contents in three kinds of form-stable PCMs were 70, 51 and 39 wt% respectively. Besides, the melting temperature and melting enthalpy of several kinds of composite PCMs were respectively within the range of 39–46 °C and 61–121 J/g. The thermal cycling test and TG analysis results show that the composite PCMs have good heat resistance and thermal stability. Furthermore, during the preparation of composite PCMs, Sari research group increased the thermal conductivity via the addition of a certain amount of expanded graphite.

$\text{SiO}_2$  and fatty acids can also be used to prepare similar composite PCMs. Fang et al. [30,85] prepared form-stable composite PCMs with flame retardant effect by using  $\text{SiO}_2$  as supporting material and fatty acids as PCMs. The sol-gel method was utilized to prepare PA/ $\text{SiO}_2$  and LA/ $\text{SiO}_2$  form-stable composite PCMs. FT-IR, XRD and SEM comprehensive characterization test results indicate that there was no chemical reaction between PA, LA and  $\text{SiO}_2$ , and PA, LA were only distributed on the pore structure of  $\text{SiO}_2$  via the capillary and surface tension function. DSC test results show that the PA/ $\text{SiO}_2$  form-stable PCMs with a PA content of 41.1 wt% had the melting temperature and latent heat of 59.76 °C and 85.11 J/g respectively, freezing temperature and latent heat of 59.20 °C and 60.55 J/g respectively. TGA test results show that the addition of melamine improved the thermal stability of the composite PCMs, playing a good flame retardant effect. There was no leakage of molten LA from the LA/ $\text{SiO}_2$  composite with a LA content of 64.8 wt%, and the LA/ $\text{SiO}_2$  composite had a melting temperature and latent heat of 42.46 °C and 117.21 J/g respectively, and a freezing temperature and latent heat of 41.30 °C and 90.00 J/g respectively. The thermal stability test results show that PA/ $\text{SiO}_2$  and LA/ $\text{SiO}_2$  composite PCMs had a good thermal stability.

Some fatty acids composites as PCMs with enhanced heat conduction property, such as form-stable PCMs prepared with

the aforesaid expanded graphite, activated carbon, silica fume and activated montmorillonite as supporting materials, also belong to PCMs prepared by virtue of porous medium's absorption.

### 3.2.2. Fatty acid and polymer mixtures as PCMs

For form-stable PCMs prepared via the mixing of fatty acids and polymer materials, there is no need to encapsulate the PCMs, which would effectively reduce the preparation cost.

Sari et al. [26] prepared a series of form-stable composite PCMs under the condition of taking Methyl Methacrylate Methacrylic Acid Copolymer (Eudragit S) as the matrix and taking fatty acids (stearic acid (SA), palmitic acid (PA), and myristic acid (MA)) as PCMs by solution casting method. Based on the research of fatty acids/Eudragit S form-stable PCMs, Kaygusuz [86] used acrylic resin Eudragit E as supporting material to prepare SA/Eudragit E, PA/Eudragit E and MA/Eudragit E form-stable PCMs, whose performance was basically with that of the form-stable PCMs with Eudragit S as the matrix. Comparison results show that the form-stable PCMs with Eudragit S as the matrix had a higher enthalpy of phase change.

Sari et al. [87] encapsulated fatty acids in the supporting material styrene maleic anhydride copolymer (SMA) to prepare a series of SMA/fatty acids form-stable composite PCMs (SMA/SA, SMA/PA, SMA/MA, SMA/LA). The encapsulation ratio of fatty acids was up to 85 wt%; furthermore, when the temperature was higher than the melting temperature of the fatty acids, there was no leakage of fatty acids. FT-IR characterization test results show that SMA was physically and chemically compatible with the fatty acids. DSC test results show that the changes in the melting and freezing temperatures of SMA/SA, SMA/PA, SMA/MA and SMA/LA were 0.48, −0.41, −0.69 and −0.66 °C, and 0.32, −0.61, −0.42 and −0.42 °C respectively compared to pure fatty acids, which can be considered as being caused by the mutual action of functional groups between SMA and fatty acids.

Wang et al. [16] prepared and performed characterization tests on form-stable fatty acid eutectic mixture/polymethyl methacrylate (PMMA) PCMs. They utilized the auto polymerization method to prepare form-stable CA-LA, CA-MA, CA-SA and LA-MA eutectic mixture/PMMA composite PCMs with a mass ratio of 50:50. The latent heat of the composite PCMs increased as the increase of LA-MA eutectic, while the compression strength decreased as the increase of LA-MA eutectic. SEM diagram shows that the four kinds of eutectic mixtures of fatty acids can be well immersed in PMMA, which effectively prevented the leakage of PCMs in the molten state. FT-IR results indicate that there was no chemical reaction between PMMA and the fatty acids. Furthermore, DSC results show that the phase change temperature and phase change enthalpy of the PCMs were 21.11 °C, 25.16 °C, 26.38 °C and 34.81 °C; 76.3 J/g, 69.32 J/g, 59.29 J/g and 80.75 J/g respectively. The difference between the tested phase change enthalpy values and theoretical calculated values were −1.0%, −0.4%, −3.3% and −0.5% respectively. The decrease of phase change temperature and latent heat was mainly caused by the mutual action of hydrogen bond between the fatty acids and PMMA.

Alkan et al. [18] encapsulated fatty acids in poly (methyl methacrylate) (PMMA) through the solution casting method to prepare a series form-stable fatty acid/PMMA (SA, PA, MA, LA/PMMA) composite PCMs. The observation results via the optical microscope show that the fatty acids were encapsulated by PMMA. FT-IR results indicate that there was a good compatibility between PMMA and the fatty acids. The thermal property study shows that the latent heat storage performance of the composite PCMs increased as the increase the fatty acids. And in the test of phase change temperatures of pure fatty acids and fatty acids/PMMA composite PCMs, there were a little changes between them, which

was caused by the mutual function of functional groups between PMMA and the fatty acids.

Sari et al. [88,89] respectively took poly (vinyl chloride) (PVC) and poly (vinyl alcohol) (PVA) as supporting materials, fatty acids (LA, MA, PA, SA) as PCMs to prepare a series of form-stable composites with different contents of fatty acids. It was found that PVC and PVA had a maximum absorption rate of 50 wt% on the fatty acids, and there was no leakage of the fatty acids in the molten state. The micrograms of form-stable PCMs show that the fatty acids were distributed in the mesh structure of PVC and PVA. The IR results of MA/PVC and LA/PVA prove that the reason why the fatty acid can be dissolved in PVC and PVA is that there exists polar groups between the fatty acids and polymer, thus there exists dipole–dipole mutual function and hydrogen bond function. Compared to pure fatty acids, the melting and freezing temperatures of composite PCMs slightly decreased, but the phase change temperature of the fatty acid/PVA composite PCMs was higher than that of homogeneous fatty acid/PVC composite PCMs with the same mass ratio. The enthalpy of phase change of the fatty acid/PVC composite PCMs and fatty acid/PVA composite PCMs was larger than the theoretical calculated value.

Sari et al. [90,91] respectively prepared two kinds of new polymer solid–solid phase change materials (SSPCMs) polystyrene-graft-palmitic acid copolymers and poly (styrene-co-ally alcohol)-graft-stearic acid copolymers by the graft copolymerization reaction. Compared with pure PA and SA, the phase change temperature of copolymer greatly decreased. Furthermore, the thermal conductivity of polymer increased as the increase of PA and SA.

### 3.2.3. Electrospun composite PCMs

In recent years, making PCM/polymer composites superfine fiber by use of the electrospun technique has become a new method to prepare form-stable PCMs. Since the composite fiber has a good stability, the electrospun technique-based fatty acid and fiber composite has a certain application prospect as a form-stable phase change material.

Chen et al. [92,93] prepared a series of form-stable polyethylene terephthalate (PET)/fatty acids (LA, MA, PA, SA) composite PCMs by use of the electrospun technique. It was found that the average diameter of LA/PET composite fiber increased with the increase of LA in the fatty acids and the diameter varied from dozens to hundreds nanometers. The SEM diagrams of electrospinning PET fiber and LA/PET composite fiber show that the two materials presented a cylindrical structure with smooth surface, which reflected a good compatibility of LA and PET in the composite fiber to some extent. The melting enthalpy values of the four LA/PET, MA/PET, PA/PET, SA/PET composite fibers with a mass ratio of 70:100 were 54.91, 60.99, 66.91 and 67.88 J/g respectively, and the freezing enthalpy values were 51.93, 55.93, 58.65 and 61.62 J/g respectively. The test results show that the melting and freezing enthalpy values of LA/PET composite fiber were smaller than those of pure LA and increased with the increase of LA, and there was no obvious change in the melting and freezing temperatures. All the phase change enthalpy values of the four composite PCMs were lower than the theoretical calculated values, which was mainly because that the manufacturing process of electrospinning affected the crystallization process of the fatty acids.

Chen et al. [94] prepared butyl stearate (SS) solid–liquid PCMs through esterification, prepared form-stable superfine SS/PET composite fiber by the method of electrospinning; and carried out a study on SS structure, and the characteristics and thermal properties of SS/PET composite fiber through FT-IR, FE-SEM and DSC techniques. The average diameter of SS/PET composite fiber increased with the increase of SS content and when the mass ratio of SS/PET was 50:100, the diameter was approximate to 1  $\mu\text{m}$ .

After 100 thermal cycling, the SEM diagram of SS/PET composite fiber show that there was no obvious change in its shape and diameter and DSC test results show that there was no obvious change in the phase change temperature before and after the cycles. The latent heat change was less than 9% after 100 thermal cycles, which reflected an excellent dimensional stability and thermal reliability of SS/PET composite fiber to some extent. The phase change enthalpy value of SS was 172.7 J/g and the phase change enthalpy value of SS/PET composite fiber with a mass ratio of 50/100 was 53.77 J/g.

Cai et al. [95] prepared a superfine composite fiber containing lauric acid (LA), polyethylene terephthalate (PET) and silica nanoparticles (nano-SiO<sub>2</sub>) through the electrospinning technique and carried out a study of the influence of Nano-SiO<sub>2</sub> on the microstructure, heat storage, thermal stability and combustion performance of LA/PET/SiO<sub>2</sub> composite fiber. Cai et al. [23] firstly prepared five eutectic mixtures of fatty acids, LA-MA, LA-PA, MA-PA, MA-SA and PA-SA and prepared a series of form-stable eutectic mixtures of fatty acids/PET superfine composite phase change fibers through the electrospinning method with PET at different mass ratio (50/100, 70/100, 100/100, 120/100). The enthalpy of fusion and crystallization of the composite fiber increased with the increase of the eutectic mixtures and there was no big change in the phase change temperature. TGA test results show that there was a good thermal stability at a lower temperature in eutectic mixtures of fatty acids/PET superfine composite fiber.

Apart from good mechanical, thermal, chemical and electrospinning properties in PET, polyamide 6 is also a good material for electrospinning. Cai et al. [96] also adopted the electrospun technique to prepare a series of lauric acid/polyamide6 (LA/PA6) superfine fiber form-stable PCMs with different mass ratio (80/100, 100/100, 120/100, and 150/100) with polyamide6 (PA6) as leaking proof material and LA as PCMs. Cai et al. [97], using a series of capric acid (CA) eutectic mixtures as PCMs, PA6 nanofiber prepared by electrospun as the form-stable material prepared a series of CA eutectic mixture/PA6 composite PCMs by virtue of the physisorption of PA fiber surface on the series CA eutectic mixtures.

### 3.2.4. Microencapsulated composite PCMs

PCM microencapsulation, as one of the methods to realize the permanent setting and freezing of PCMs, can effectively solve the problems of leaking, phase separation and corrosivity of PCMs, overcoming the limitation of direct application of PCMs and expanding the application area of PCMs. In the manufacturing of phase change microcapsules, organic high polymers, such as gelatin-Arabic gum, melamine resin, poly(methyl methacrylate) PMMA and polycarbonate (PC) are often adopted as wall materials.

Ozonur et al. [98] adopted natural coco fatty acid mixture which is cheap and easy to get as the core material to prepare phase change microcapsules with gelatin-Arabic gum as the shell material and a grain diameter of 1 mm via the coagulation technique. The FT-IR characterization test results show that the coco fatty acid microcapsules remained its chemical structure after microencapsulation. Compared with the coco fatty acid, the microcapsules had decreased heat absorption rate and heat release rate, and increased phase change temperature. Bao et al. [99] made use of the in-situ polymerization method to prepare phase change microcapsules with LA as the core and melamine formaldehyde (MF) resin as the shell material. The SEM test results show that the microcapsules were in the shape of balls with a smooth surface and a grain size of about 400–500  $\mu\text{m}$ , and the shell material presented a round shell layer associated with an inner porous structure. After the composite materials underwent 70 thermal cycles, in the corresponding SEM

diagram, it could be found that there were fractures on some microcapsules. DSC test results show that the melting temperature and melting enthalpy value of pure LA were 44.9 °C and 183.8 J/g respectively and the melting temperature and melting enthalpy of LA/FM phase change microcapsules were 43.7 °C and 83.96 J/g respectively. After the microcapsules underwent 70 cold and thermal cycles, the phase change temperature and phase change enthalpy value were 42.4 °C and 77.06 J/g. The decrease in the enthalpy value of the microcapsules after 70 cycles was the result of the leaking of part of LA resulted from the fracture of shells. Therefore, the process of microencapsulation must be optimized and the cross-linking of the shell material must be improved so as to ensure a good integrity of the shell.

Wang et al. [100] prepared form-stable SA/PMMA composite phase change microcapsules with a shell structure by adopting ultraviolet curing dispersion polymerization. The SA/PMMA microcapsules had a single phase surface, a regular spherical structure, a grain size of 2–3 μm and a smooth surface. No chemical reaction happened between PMMA and SA, which showed a good compatibility. The melting and freezing phase change temperatures of pure SA were 54.2 °C and 54.9 °C respectively, and such temperatures of the composite material were 54.8 °C and 53.8 °C respectively. The melting and freezing latent heat values of SA were 177.8 J/g and 185.6 J/g respectively, and such values of the form-stable composite material were 92.1 J/g and 95.9 J/g respectively. The encapsulation ratio of the composite material was 51.8%. DSC and FT-IR characterization test results show a good thermal and chemical stability of SA/PMMA composite material. Zhang et al. [101] also prepared stearic acid/polycarbonate microencapsulated PCM with SA as the core material via the solution casting method. Its form, chemical structure and heat properties were characterized by means of SEM, FT-IR, DSC, temperature curve and coefficient of cubical expansion. SA with the largest mass fraction of 52% was encapsulated by the composite material to prevent leaking. The average grain size of the phase change microcapsules was 0.5 μm. There was no chemical reaction between SA and PC, which showed a good compatibility. The melting and freezing temperatures and latent heats of SA/PC microcapsules were 60.0 °C and 51.2 °C, 91.4 J/g and 96.8 J/g respectively. Studies found that the rate of heat storage and heat release of the composite material with 3 wt% iron powder added was increased by 23% which effectively improved the phase change rate of the composite material. These form-stable SA/PC microcapsules, which can be prepared easily and has a good thermal stability, can be used as a candidate PCM to be applied in the heat storage area.

In addition, the inorganic high polymer has also become a research hot spot as the shell material of phase change microcapsules. Chai et al. [102] adopted the low-heat solid state reaction to prepare stearic acid/silica (SA/SiO<sub>2</sub>) phase change microcapsules. They adopted infrared spectrum, X-ray diffraction and differential scanning calorimetry to characterize SA/SiO<sub>2</sub> phase change microcapsules and measured the size distribution of the microcapsules with the dynamic light scattering laser particle size analyzer. SA/SiO<sub>2</sub> phase change microcapsules had a ball structure with a grain size of 110 nm. The phase change temperature and latent heat of SA/SiO<sub>2</sub> phase change microcapsules were 64 °C and 153.3 J/g respectively. Pan and others [103] adopted the in-situ emulsion interfacial poly-condensation method to prepare a new microencapsulated phase change material (palmitic acid@AlOOH). This colloidal microcapsule had a grain size around 200 nm and a core-shell microstructure. IR characterization test results show a relatively strong interfacial interaction between PA and AlOOH. TGA test results show the contents of PA in the microcapsules were 52 wt%, 57 wt% and 69 wt% respectively. The thermal conductivity coefficients of the three composite materials and PA were 0.84, 0.74, 0.70 and 0.16 W/m K respectively. The shell AlOOH with relatively

good thermal conductivity improved the thermal conductivity of the composite material.

#### 4. Fatty acids as PCMs for energy storage system

##### 4.1. Wallboard with PCM energy storage system

Phase change wallboards, as the combination of fatty acids as PCMs and basic building materials, can reduce the temperature fluctuation range in a room and improve the comfort of the indoor environment as well as take effect in energy efficiency and environmental protection.

Karaipekli and Sari [17] made use of CA-PA eutectic mixture and gypsum powder to prepare phase change wallboards (PCWs), in which the purity of CA and PA were 98% and 96% respectively. The research found that the maximum ratio of the eutectic mixture of fatty acids was 25% and the melting point and freezing point of PCWs made in that ratio were 22.94 °C and 21.66 °C respectively and the melting and freezing heat were 42.54 J/g and 42.18 J/g respectively. After 5000 thermal cycles, no leaking was found and the melting point and freezing point turned to be 22.74 °C and 21.24 °C with the melting heat and freezing heat changed to be 41.16 J/g and 40.63 J/g respectively, which showed a relatively good thermal reliability.

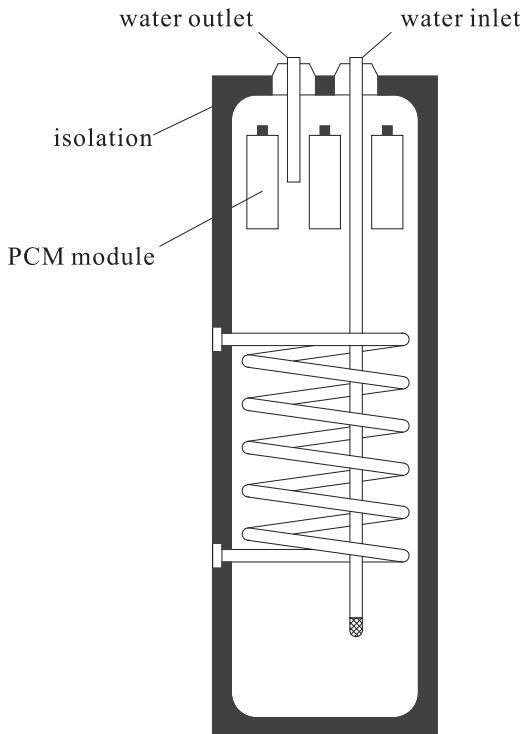
Lv et al. [13] made use of CA-LA eutectic mixture and plaster slabs to prepare PCWs. In the process of preparation, the melting points of CA and LA elementary substances used were 30.638 °C and 42.906 °C respectively and the latent heat values were 155.457 J/g and 175.832 J/g respectively. The phase change temperature of CA-LA eutectic mixture prepared was 19.67 °C and its latent heat was 126.562 J/g. The thermal conductivity of PCWs was 0.21 W/m K, which was 0.17 W/m K higher than that of the plaster slab. The melting point and latent heat of PCW were 19.108 °C and 35.239 J/g respectively, which turned to be 18.353 °C and 35.068 J/g after 360 cycling. Lv et al. [104,105] also made a comparison between the room with ordinary wallboard and that with PCWs in Northeast China in winter. The thickness of plaster slabs was 9.5 mm and the mass ratio of the PCM was 26%. The house in test was a 5 m × 3.3 m × 2.8 m room with a 1.5 × 1.5 m<sup>2</sup> window in the south wall and a 1 m × 2 m wooden door in the north wall.

Neeper [106] studied the dynamic heat transfer characteristics of the wallboards made of fatty acid/paraffin wax mixture and the plaster. The study found that the energy storage capacity of PCWs depended on the melting point and phase change temperature range of the PCM, and latent capacity per unit area of wallboard. The maximum energy storage capacity occurred when the melting point of the PCM was close to the average indoor temperature. And the maximum energy storage capacity was 300–400 kJ/m<sup>2</sup> every day.

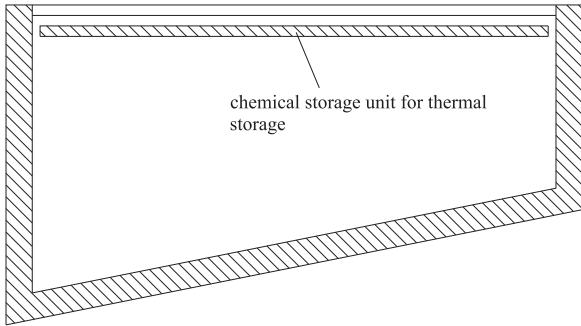
##### 4.2. Solar heat storage and photovoltaic system

Hamid [107] put forward a kind of solar latent heat storage unit (LHSU) consisting of a series of identical tubes embedded in PCMs, a solar collector and a phase change energy storage unit. In the charging mode, hot water from the solar collector passes through the tubes and transfers the collected heat of solar radiation to PCMs. The heat stored in the liquid PCMs is then transferred to water in the discharging mode to provide hot water. Hamid, based on the finite volume method, established the mathematical model for the system and studied the optimization design of the phase change unit of SA. The optimization design includes the quality of PCMs, number of units, and water flow.

Mazman [108] arranged cylinder phase change units above the solar domestic hot water tank (Fig. 2), and filled the units with



**Fig. 2.** Solar domestic hot water tank.



**Fig. 3.** Cross-sectional views of built-in storage solar water heaters.

paraffin and palmitic acid (PP), paraffin and stearic acid (PS), stearic acid and myristic acid (SM) respectively with the ratio of 80 wt%:20 wt% for each unit. Graphite (10%) was added into the PCM. The volume of the tank was 150 L, and the dimensions were 0.125 m in height and 0.78 m in diameter. In the work, the effect of PCM modules in the stratified solar domestic hot water (SDHW) tank was investigated. In the cooling experiments, the average tank water temperature dropped below the melting temperature of the PCM in 6–12 h from 65 to 68 °C. In the heating experiments, 3 kg of PCM could increase the temperature of 14–36 L water at the upper part of the SDHW tank by 3–4 °C.

Tarhan and Sari [109] studied the application of fatty acids in the built-in storage solar water heaters (BSSWHs). The schematic diagram of BSSWHs is shown in Fig. 3. In their analysis of two fatty acids, LA and MA, respectively, they found that LA heat storage system was more effective in the daytime, thus able to save the volume of the water tank; while MA heat storage unit was more effective in the nighttime, for it had a higher melting temperature and a lower solid phase thermal conductivity.

Fatty acids as PCMs have also been applied in the building integrated photovoltaics (BIPV). The temperature of the BIPV can affect the photovoltaic efficiency. Generally speaking, whenever the temperature rises by 1 °C, the efficiency will decrease by 0.4–0.6%.

Fatty acids as PCMs can be used to absorb the heat of the BIPV, controlling the temperature rise so as to improve the photovoltaic efficiency. Hasan [110] studied the performances of five kinds of PCM/BIPV composites formed by fatty acids as PCMs including the eutectic mixture of CA and LA and the eutectic mixture of CA and PA, and BIPV. The results show that the performance of PCM/BIPV structure was influenced by the mass ratio and thermal conductivity of the PCM, where the thermal conductivity of the PCM container had a larger influence on the performance of PCM/BIPV structure. Under the ambient temperature of 34 °C and a solar radiation intensity of 1000 W/m<sup>2</sup>, it is practicable to apply the eutectic mixture of CA and PA and CaCl<sub>2</sub> · 6H<sub>2</sub>O to BIPV for both materials can keep the temperature of PV at 18 °C in half an hour.

#### 4.3. Condensing heat recovery of the air conditioning system

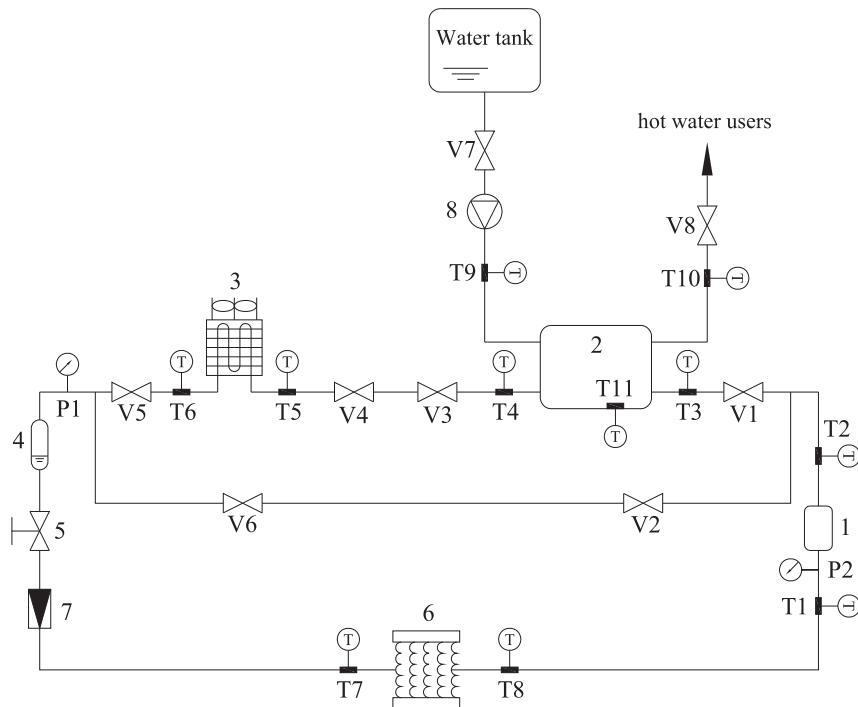
The compression refrigerating unit as well as chillers unit with absorption or similar technology will discharge a great amount of condensation heat to the air under refrigerating conditions. Heating of domestic water by condensing heat can not only save energy consumption, but also reduce the environmental warming caused by the heat discharged by the air conditioning system. As the heat discharged by the unit in operation is out of sync with the demands, it is necessary to set a heat storage device, which is suitable for both seasonal storage to heating loads and daily storage for domestic hot water preparation. Since the conventional storage tanks occupy a large area for energy storage and have a low efficiency of heat exchange, researchers have attempted to use phase change heat storage to recover condensing heat in the air conditioning system [111–114].

According to the current researches, there are three kinds of phase change heat accumulators to recover condensing heat.

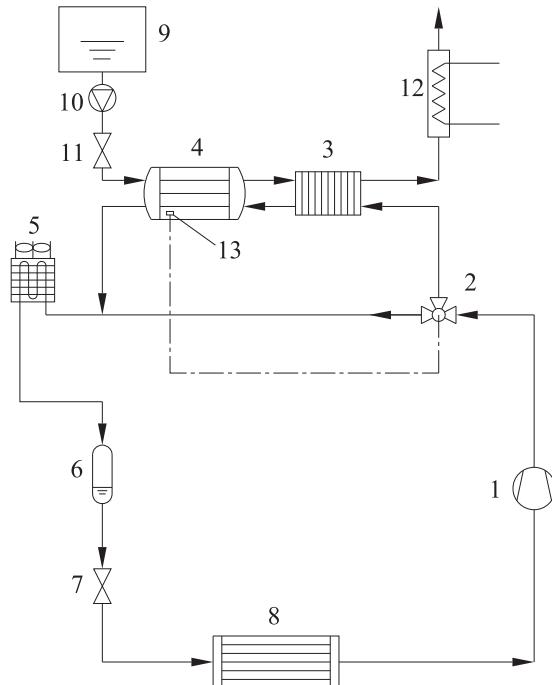
One is to install in series a phase change heat accumulator to the condenser in the air conditioning unit circuit. Liu [111] installed a heat storage tank on the exterior of the self-designed finned-tube heat exchange, as shown in Fig. 3. PCMs are stored between the shell and the finned-tube, and the cold and hot fluid flows through the tube respectively. If domestic hot water is needed, the valve can be opened to have the tap water or water in the tank flow into the phase change heat accumulator for heat exchange with PCMs in the heat accumulator; if the hotter water is needed, auxiliary electric heater can be used for further heating. Fig. 4.

Another is to install in series a high-temperature phase change heat accumulator and a low-temperature phase change heat accumulator to the condenser in the air conditioning unit circuit [113]. The refrigerator comes out of the compressor, and then goes through the high-temperature phase change heat accumulator and the low-temperature phase change heat accumulator successively; while the cold water goes through the low-temperature phase change heat accumulator and the high-temperature phase change heat accumulator successively, becoming domestic hot water after twice heating. The thermal energy recovery system consists of a conventional air conditioning system, two heat recovery accumulators and an auxiliary electric water heater, as shown in Fig. 5.

The third is to install in series a phase change heat accumulator and a water heat accumulator to the condenser in the air conditioning unit circuit [114] (as shown in Fig. 6). Wherein, the heat accumulating temperature of the phase change heat accumulator is 50–60 °C, fully using the high latent heat of PCMs for condensing heat recovery. The temperature for the water heat storage is controlled at 45 °C. If the refrigerant from the water heat accumulator has a temperature over 45 °C, the refrigerant needs to be further cooled in the condenser. The whole equipment consists of compressor, air-cooled condenser, phase change heat storage device, reservoir, electronic expansion valve, evaporator, electric heater, and auxiliary equipment.



**Fig. 4.** Thermal energy recovery system of air conditioning system with phase change heat accumulators. 1. Compressor, 2. Accumulator, 3. Air-cooled condenser, 4. Liquid storage tower, 5. Restrictive valve, 6. Air-cooled evaporator, 7. Flow meter, 8. Blower pump, P1, P2. Pressure gauge, V1-V8. Valve, T1-T11. Digital thermometer.

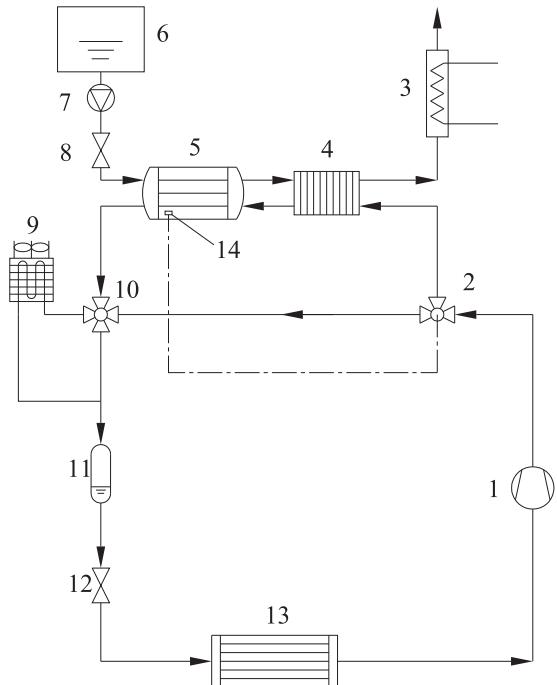


**Fig. 5.** Schematics of the air conditioning system with a high-temperature phase change heat accumulator and a low-temperature phase change heat accumulator. 1. Compressor, 2. Three-way valve, 3. Higher temperature accumulators, 4. Lower temperature accumulators, 5. Cooling tower, 6. Liquid storage tower, 7. Valve, 8. Evaporator, 9. Tap water tank, 10. Water pump, 11. Tap water valve, 12. Auxiliary electrical heater, and 13. Temperature sensor.

## 5. Discussions and conclusions

### 5.1. Eutectic mixture of fatty acids

The phase change temperature and latent heat of fatty acids are increasing with the increase of the carbon chain length. There are



**Fig. 6.** Schematics of the air conditioning system with a phase change heat accumulator and a water heat accumulator. 1. Compressor, 2. Three-way valve, 3. Electrical heater 4. High temperature phase change heat accumulator, 5. Heat storage water tank, 6. Water tank, 7. Water pump, 8. Valve, 9. Condenser, 10. Four-way valve, 11. Liquid storage tower, 12. Restrictive valve, 13. Evaporator, and 14. Temperature sensor.

many advantages of fatty acids as phase change materials. Besides those advantages, the eutectic mixtures of fatty acids have a better heat reliability, and moreover the binary and ternary fatty acid eutectic mixtures have lower phase change temperatures as compared with the corresponding fatty acids. This can greatly enrich the phase change temperature system of fatty acid phase change

materials (PCMs) and expand the engineering application background of fatty acids.

### 5.2. Thermal reliability and stability of fatty acids

The present researches are to analyze the heat reliability of fatty acids based on the comparison of the phase change temperature and latent heat of fatty acids as PCMs after repeated cycles. According to the research results, fatty acids as PCMs have a good thermal reliability, and the reason for the change of latent heat and phase change temperature is that PCMs are not pure, that is, the existence of impurities affects the latent heat and phase change temperature. However, the research results show that there were no regular patterns for the change of latent heat and temperature of phase change and also the influencing mechanism of impurities was unclear. The thermal stability of fatty acids was influenced by the polymorphism of the fatty acids; the chemical stability of saturated long-chain carbon structure of the fatty acids accounted for the thermal stability of fatty acids.

### 5.3. The increase of thermal conductivity and the setting of PCMs

As fatty acids as PCMs have a poor thermal conductivity, they should be made, together with the materials of high thermal conductivity, into composite PCMs. On the other hand, the realization of permanent setting and solidification of PCMs have many benefits, such as no need for additional encapsulation, cost-effectiveness, stable shape, and readiness for applications with tunable dimension. Hence, it should be the key direction of development to combine PCMs with expanded graphite (EG), activated carbon, silica fume (SF) and activated montmorillonite ( $\alpha$ -MMT) and others to form composite PCMs with a stable form and a good thermal conductivity.

### 5.4. Phase change energy accumulator

The application of fatty acids in engineering is mostly in the form of phase change energy accumulators. At present, there are only a few studies on this aspect. There should be wider and deeper numerical calculation and experimental researches in the operating characteristics of phase change energy accumulators, based on which, a wider and deeper research on structural optimization is necessary.

### 5.5. Thermal properties of fatty acids

The researches in thermal properties of fatty acids are mainly focused on DSC-based tests of phase change temperature and latent heat. It is required to have a further research on the heat transfer and flow of PCMs in composite PCMs and their plates and microcapsules, and in the heat transfer characteristics of PCMs in phase change units and phase change energy accumulators.

### 5.6. Applications of the fatty acids

Thermal energy storage is an efficient way to improve the energy utilization efficiency. Latent heat storage is realized by absorbing and releasing latent heat during the phase change process of PCMs. Fatty acids as PCMs have been applied in several energy storage applications such as wallboard with the PCM energy storage system, the solar heat storage and photovoltaic system, condensing heat recovery of the air conditioning system. They also can be applied in temperature adaptable greenhouses, thermo-regulating fibers or smart textile materials, etc.

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